

PATENT SPECIFICATION

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SPECIFICATION NO. 1,017,959

The inventors of this invention in the sense of being the actual devisers th within the meaning of Section 16 of the Patents Act, 1949 are:— Ernst Podschus, Driescher Hecke 27, Leverkusen, Germany, Werner Joseph, Gronauer Strasse 41, Koln-Mulheim, Germany, both of German nationality.

THE PATENT OFFICE

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larly described in and by the following statement:—

- 10 This invention relates to a process for the production of a new type of calcined clay pigments.

- It is known that silicates of the alkaline earth metals and of aluminium are used in various materials as fillers. They have an extremely good brightening effect in systems where the boundary surface is provided by filler and air, for example in paper, and in size paints or lean dispersion paints. When dispersed in materials having a higher light-refractive power, as for example in synthetic plastics or lacquers, they are not able to have a covering effect because of their low refractive exponent. Most of the silicates used as fillers are clay minerals, of which kaolin is especially important as the pigmenting properties can be improved by calcination. As compared with the uncalcined kaolins, the calcination products after a heat treatment at about 1000°C. show a higher degree of brightness and a higher brightening power.

- It is also known (see British Patent Specification No. 869966) that rapid heating of kaolin and other layer lattice silicates in a stream of hot gas having high turbulence to about 700 to 900°C. yields products with a considerably higher adsorption power as compared with untreated kaolin. Such products are for example very suitable as support materials for liquid active substances e.g. pesticides and also as grinding auxiliaries and free flowing means for cak-

for the production of calcined clay pigments, by calcination of clays containing water of hydration, wherein

a) the clay is heated in a highly turbulent hot gas stream for a period of 1 second or less, to a temperature of from 600 to 1000°C. and

b) the heated product is thereafter heated for at least 10 minutes at 800 to 1100°C in the absence of chlorine.

The clay preferably is first of all heated in a highly turbulent hot gas stream to 700 to 900°C., and then preferably subjected to a calcination at 900 to 1000°C.

The heating methods used in the invention mainly differ as regards the heating period and temperature. The shock calcination effected in the first stage, causes the major part of the water of hydration in the aluminium silicate to be split off. The product formed is amorphous to X-rays, is substantially looser than the starting material and also considerably looser than products which are obtained by longer heat treatment at the same temperature. The product obtained by shock calcination consequently has a higher adsorption power than the products produced by conventional calcination processes. It should be noted that the brightness of kaolin subjected only to shock calcination leaves something to be desired as compared with products produced by longer heat treatment in a calcining furnace at similar temperatures.

It has now surprisingly been found that by a combination of both calcining methods

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COMPLETE SPECIFICATION

NO DRAWINGS

A Process for the Production of New Calcined Clay Pigments

We, **FARBENFABRIKEN BAYER AKTIEN-GESELLSCHAFT** of Leverkusen-Bayerwerk, Germany, a body corporate organised under the laws of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to a process for the production of a new type of calcined clay pigments.

It is known that silicates of the alkaline earth metals and of aluminium are used in various materials as fillers. They have an extremely good brightening effect in systems where the boundary surface is provided by filler and air, for example in paper, and in size paints or lean dispersion paints. When dispersed in materials having a higher light-refractive power, as for example in synthetic plastics or lacquers, they are not able to have a covering effect because of their low refractive exponent. Most of the silicates used as fillers are clay minerals, of which kaolin is especially important as the pigmenting properties can be improved by calcination. As compared with the uncalcined kaolins, the calcination products after a heat treatment at about 1000°C. show a higher degree of brightness and a higher brightening power.

It is also known (see British Patent Specification No. 869966) that rapid heating of kaolin and other layer lattice silicates in a stream of hot gas having high turbulence to about 700 to 900°C. yields products with a considerably higher adsorption power as compared with untreated kaolin. Such products are for example very suitable as support materials for liquid active substances e.g. pesticides and also as grinding auxiliaries and free flowing means for cak-

ing substances.

It has also already been proposed (see British Patent Specification No. 894383) to subject kaolin to shock heating and thereafter to bleach it by treatment with chlorine gas at 700 to 900°C.

The present invention provides a process for the production of calcined clay pigments, by calcination of clays containing water of hydration, wherein

a) the clay is heated in a highly turbulent hot gas stream for a period of 1 second or less, to a temperature of from 600 to 1000°C. and

b) the heated product is thereafter heated for at least 10 minutes at 800 to 1100°C in the absence of chlorine.

The clay preferably is first of all heated in a highly turbulent hot gas stream to 700 to 900°C., and then preferably subjected to a calcination at 900 to 1000°C.

The heating methods used in the invention mainly differ as regards the heating period and temperature. The shock calcination effected in the first stage, causes the major part of the water of hydration in the aluminium silicate to be split off. The product formed is amorphous to X-rays, is substantially looser than the starting material and also considerably looser than products which are obtained by longer heat treatment at the same temperature. The product obtained by shock calcination consequently has a higher adsorption power than the products produced by conventional calcination processes. It should be noted that the brightness of kaolin subjected only to shock calcination leaves something to be desired as compared with products produced by longer heat treatment in a calcining furnace at similar temperatures.

It has now surprisingly been found that by a combination of both calcining methods

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according to the invention, products are obtained which have a higher degree of brightness and excellent pigmenting properties. The pigmenting properties of the products produced by the process of the invention, (for example when using kaolin), are clearly better than those of the prior known calcination products, which were produced by longer calcination of kaolin at for example 1000°C.

In the present process, the shock heating can be effected in an apparatus such as that described in British Patent Specification No. 869966. The stream of hot gas generated for example by burning illuminating gas enters a conical reaction chamber tangentially at the bottom end thereof at high velocity. The clay to be heated is introduced as dust into the axial return flow caused by the conical shape of the apparatus. In the zone of high turbulence in the boundary layers between the tangential upward flow and the axial return flow, the clay is heated in finely divided form for one second or less. The calcination product leaves the reaction chamber with the gases tangentially at the upper end and is separated out, e.g. in a following cyclone.

The heating step (b) at 900 to 1100°C. can be effected in conventional furnaces, for example rotary furnaces, drum furnaces or muffle furnaces. The shock calcination product of the first stage after being separated (e.g. in the cyclone) is preferably conducted while still hot into the second heating stage. A cooling of the flash calcined material is only effected, for example by means of heat exchangers for preheating the air for combustion, to the extent which is necessary for increasing the degree of separation.

The pigments produced according to the invention are whiter, not only as a powder but also when used in paper or paper coating and in other size coatings than the prior known products obtained at about 1000°C. by calcination of high-grade kaolin; they also show a surprisingly high brightening power when they are dispersed in substances with higher light refraction power, this not being the case with the prior known silicate pigments. The difference in the whiteness between the pigment produced according to the invention and the prior known calcination product is substantially greater if the comparison is carried out not in the powder or size coating, but for example in a linseed oil dispersion. The pigment produced according to the invention appears white, whereas the hitherto usual calcined clay pigments appear yellowish brown. This difference is very surprising, since the products show no appreciable difference, neither in composition nor in light-refraction power.

The pigments produced according to the invention have a lower density, e.g. a specific gravity of about 1.5 to 2.0 (when determined in a Pyknometer, e.g. in benzene or in water) than the products heat-treated in the hitherto usual manner. Such products heated in the usual manner have a specific gravity of about 2.4 after calcining in a muffle furnace, whereas uncalcined kaolin has a value of about 2.6. It may consequently be assumed that the products of the invention contain gas-filled cavities into which the embedding agent is not able to penetrate. Whereas only the boundary surface between the pigment and embedding medium is considered with the prior known pigments for the light dispersion, there is also the boundary surface between pigment and gas with the products according to the invention. At the boundary surface between pigment and embedding medium, the light dispersion is low if the refraction exponents only differ slightly from one another, as is the case for example with normally calcined clay in oil and lacquers. On the contrary, at the boundary surface between pigment and air there is strong dispersion.

The particle size distribution according to the method of Andreasen indicates that the maximum size of the particles is $<4\mu$ in diameter.

As compared with prior known calcined clay pigments, the new pigments have the advantage of better whiteness, higher brightening power, especially in media with refractive exponents or indices in the range of 1.5 and a lower specific gravity. Accordingly, they are also suitable for brightening substances, such as synthetic plastics and rubber, and also for producing paints with good covering power which are based on dispersion binders and oils and lacquers; in many cases, they can replace the more expensive pigments with a high refractive index, such as titanium dioxide and zinc sulphide, or they can be used as an additive to these pigments.

The following Examples illustrate the invention, the percentages being by weight:

Example 1

A high-grade finely dispersed elutriated kaolin of following composition

45.20%	of SiO_2	
38.75%	of Al_2O_3	
0.33%	of Fe_2O_3	
1.64%	of TiO_2	
0.09%	of MgO	
0.28%	of Na_2O	
0.05%	of K_2O	
14.04%	of heat loss	

was treated at different temperatures by shock heating, by a calcining process lasting for one hour in a muffle furnace, and by the combined calcination process according to the invention.

Calcination		Temp. °C.	Bulk density g/l	Remission at	
				420m μ	570m μ
1)	shock calcination	800	296	76.8	92.1
1a)	Muffle furnace	800	538	81.2	93.4
5 1b)	Shock calcination + Muffle furnace	800+1000	340	89.2	95.7
2)	Shock calcination	900	332	78.8	92.3
2a)	Muffle furnace	900	535	83.2	93.8
2b)	Shock calcination + Muffle furnace	900+1000	345	89.7	95.9
10 3)	Shock calcination	1000	487	78.8	92.2
3a)	Muffle furnace	1000	580	87.9	95.4
4)	Shock calcination	1100	625	76.8	91.1
4a)	Muffle furnace	1100	603	88.2	95.8
15 5)	Initial Kaolin	—	545	81.1	91.3

The calcination process for one hour led in all cases to products with a substantially higher brightness. The remission values in blue with the shock-calcined specimens are even less satisfactory than in the initial kaolin. The products of the shock calcination at 800 to 900°C. (1 and 2) were subjected to a subsequent heat treatment at 1000°C. for one hour. It is seen that the combination of the two heat treatments leads to the production of pigments with higher remission values. These good properties are also maintained if the pigments are thereafter subjected to a dry-grinding or wet grinding process.

A value of about 1.8 is found for the specific gravity of the specimen 1b) (determined in a Pyknometer with benzene with evacuation for several hours); a value of about 2.4 is found for the specimen 3a). The determination of the brightening power with castor oil-ultramarine blue paste according to the German Industrial Standard, DIN 53191, shows a value 3-4 times better for the specimen 1b) treated according to the invention, by comparison with the

specimen 3a only treated in the furnace at 1000°C.

Example 2

A high-grade elutriated kaolin of the 45 composition

45.25%	of SiO ₂	
40.10%	of Al ₂ O ₃	
0.24%	of Fe ₂ O ₃	
0.41%	of TiO ₂	50
0.22%	of Na ₂ O	
0.38%	of K ₂ O	
13.44%	of heat loss	

was subjected to various calcination conditions similar to those described in Example 1. In the first series of experiments the kaolin starting material was calcined directly at 900-1000°C. in quartz dishes of about 100 grams capacity in an electrically heated muffle furnace. In the second series the kaolin starting material was heated at first to 800°C. within less than a second in the manner described. The shock calcination product was then calcined in the muffle furnace at 900 and 1000°C. Some properties of the resulting pigments are shown in the table below:

Calcination		Temp. °C.	Oil absorption, ml of lin-seed oil/g	Remission at		Bulk density g/l
				420m μ	570m μ	
70 1)	1 hour muffle furnace	900	10.2	83.2	93.3	550
2)	15 minutes muffle furnace	1000	10.1	85.0	94.0	
75 3)	1 hour muffle furnace	1000	10.1	86.3	95.0	550
4)	5 hours muffle furnace	1000	10.0	87.9	95.5	
5)	shock calcination	800	13.5	81.3	87.5	
6)	1 hour muffle furnace	900	13.5	86.1	94.5	335
7)	15 minutes muffle furnace	1000	12.5	88.2	95.3	
80 8)	1 hour muffle furnace	1000	12.3	88.7	95.8	335
9)	5 hours muffle furnace	1000	12.3	90.7	96.4	
10)	Initial Kaolin	—	6.1	80.8	98.8	650

It can be seen that the products 6) to 9) which had been subjected according to the invention first to shock calcination at 800°C. and subsequently to a prolonged calcination treatment at 900 and 1000°C. respectively,

show in all cases higher remission values, particularly in the blue region, than the samples 1) to 4) which had been calcined directly in the muffle furnace. Moreover, they are more voluminous and adsorb more

oil, as is shown by the values for the oil adsorption according to Gardner-Coleman and the bulk density. The remission values of the samples calcined at 1000°C. are higher
5 than the samples calcined at 900°C. Besides, the brightness increases as the calcination period is prolonged. The requisite calcination period depends of course on the type of the furnace and the heat transmission, in
10 this case on the size and the capacity of the quartz dishes used.

The determination of the brightening power with castor oil-ultramarine blue paste shows a value about 4 times better for the
15 samples 8) and 9) as compared with the samples 3) and 4).

WHAT WE CLAIM IS:—

1. A process for the production of calcined clay pigments, by calcination of clays
20 containing water of hydration, wherein

a) the clay is heated in a highly turbulent hot gas stream for a period of 1 second or less, to a temperature of from 600 to 1000°C. and

25 b) the heated product is thereafter

heated for at least 10 minutes at 800 to 1100°C. in the absence of gaseous chlorine.

2. A process as claimed in claim 1, wherein the clay is heated in step (a) in a highly turbulent hot gas stream to a tem- 30 perature from 700 to 900°C.

3. A process as claimed in claim 1 or claim 2, wherein the heated product is heated in step (b) to 900 to 1000°C.

4. A process as claimed in claim 1, substantially as described with reference to Example 1. 35

5. A process as claimed in claim 1, substantially as described with reference to Example 2. 40

6. Calcined clay pigments when produced by the process claimed in any of the preceding claims.

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